Adducts of Tetrachlorobenzyne and Pyrroles

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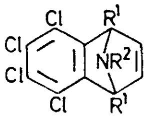
Summary Tetrachlorobenzyne adds to *N*-substituted pyrroles to give 5,6,7,8-tetrachloro-1,4-dihydronaphthalen-1,4-imines and in one case another adduct, a tetrachlorobenzo[3.4]cyclobuta[1.2-*b*]pyrrole; the naphthalen-1,4-imines decompose thermally by a retro-Diels–Alder reaction.

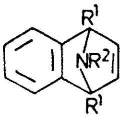
Benzyne adds to a variety of *N*-substituted pyrroles to give 1,4-dihydronaphthalen-1,4-imines or other products which arise by secondary reactions of these 1 : 1 adducts with benzyne.[1] One adduct (**1**) of the same type has been obtained using tetrachlorobenzyne.[2] However, previous attempts to add benzyne to 1,2,5-trisubstituted pyrroles gave only 2-naphthylamine derivatives, supposedly by rearrangement of the intermediate 1,4-dihydronaphthalen-1,4-imines (**4**)—(**6**).[3]

The adduct (**2**),† m.p. 182—184 °C, which we have obtained from tetrachlorobenzyne (generated from C_6Cl_6 and Bu^nLi in Et_2O) and 1,2,5-trimethylpyrrole, is thus the first 1,4,*N*-trisubstituted naphthalen-1,4-imine to be characterised. The symmetrical structure (**2**) is shown by the ^1H n.m.r. spectrum [τ 3·50 (2H, s, CH=CH), 8·05 (3H, s, NMe), and 8·24 (6H, s, Me)] and by formation of the ion $MeC{\equiv}N^+$-Me (most intense peak in the mass spectrum, *m/e* 56), which is a fragmentation pattern characteristic of naphthalen-1,4-imines.[4]

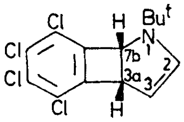
The corresponding adduct (**3**), m.p. 96—98 °C, was obtained (50% yield) from tetrachlorobenzyne and *N*-t-butylpyrrole, but in this case an isomeric product of the reaction is of greater interest. The minor adduct (2% yield), m.p. 142—144 °C, is assigned the structure (**7**), principally



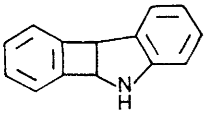
(1) $R^1 = H$, $R^2 = Me$
(2) $R^1 = R^2 = Me$
(3) $R^1 = H$, $R^2 = Bu^t$



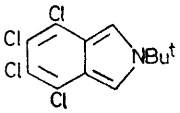
(4) $R^1 = Me$, $R^2 = PhCH_2$
(5) $R^1 = Me$, $R^2 = Ph$
(6) $R^1 = Ph$, $R^2 = Me$



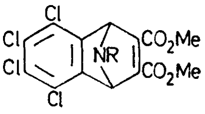
(7)



(8)



(9)



(10) $R = Bu^t$

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† All new compounds analysed correctly for C, H, and N.

on the evidence of its ^{1}H n.m.r. spectrum: τ ($CDCl_3$) 3·22 (1H, q, 2-H), 3·59 (1H, q, 3-H), 6·57 (1H, d, 7b-H), 7·31 (1H, octet, 3a-H), and 8·93 (9H, s, Bu^t); $J_{2,3}$ 10, $J_{2,3a}$ 1, $J_{3,3a}$ 4, and $J_{3a,7b}$ 6 Hz. This is apparently the first example of the benzo[3.4]cyclobuta[1.2-*b*]pyrrole ring system. Formation of a cyclobutene ring by 1,2-cycloaddition of benzyne is unusual, although benzyne and indol-1-yl-lithium gave the tetracyclic adduct (**8**) and isomeric phenylindoles.[5]

The 1,4-dihydronaphthalen-1,4-imine (**2**) was more stable than implied by the mild conditions for rearrangement of the analogous adducts (**4**)—(**6**),[3] but acetylene was evolved when (**2**) was heated above 200 °C. Compound (**3**) decomposed in the same way to give acetylene and the isoindole (**9**), m.p. 156 °C, which was converted into its adduct (**10**), m.p. 163—165 °C, with dimethyl acetylenedicarboxylate when (**3**) was heated at 200 °C with the acetylenic ester. The behaviour of the *N*-t-butylnaphthalen-1,4-imine (**3**) in this respect is very different from that of the analogous *N*-methyl derivative (**1**),[6] which gave 1,2,3,4-tetrachloronaphthalene as the main product. A precedent for the observed decomposition of compounds (**2**) and (**3**) by a retro-Diels–Alder reaction is described for 5,6,7,8-tetrafluoro-1,4-dihydro-1,4-(*N*-methylimino)naphthalene,[7] although in this case tetrafluoro-*N*-methylphthalimide was isolated rather than 4,5,6,7-tetrafluoro-2-methylisoindole.

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[1] L. J. Kricka and J. M. Vernon, *Adv. Heterocyclic Chem.*, 1974, **16**, 87, and references therein.

[2] G. W. Gribble, N. R. Easton, jun., and J. T. Eaton, *Tetrahedron Letters*, 1970, 1075.

[3] E. Wolthuis, D. V. Jagt, S. Mels, and A. DeBoer, *J. Org. Chem.*, 1965, **30**, 190.

[4] L. J. Kricka and J. M. Vernon, *J.C.S. Perkin I*, 1972, 904.

[5] M. E. Kuehne and T. Kitagawa, *J. Org. Chem.*, 1964, **29**, 1270: the u.v. spectrum of adduct (**8**) was recorded, but not the n.m.r. spectrum. There is no discussion of other evidence in support of this structural assignment.

[6] L. J. Kricka and J. M. Vernon, *Chem. Comm.*, 1971, 942.

[7] P.L. Coe and A. J. Uff, *Tetrahedon*, 1971, **27**, 4065.